Prediction of the ^{13}C NMR chemical shifts of organic species adsorbed on H-ZSM-5 zeolite by the ONIOM-GIAO method†

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The ONIOM-GIAO method has been used to accurately predict ^{13}C NMR chemical shifts for a series of organic species adsorbed on H-ZSM-5 zeolite. This is useful for the spectroscopic identification of complicated catalytic systems.

The catalytic conversions of methanol to hydrocarbons, including methanol-to-gasoline (MTG) and methanol-to-olefin (MTO) on solid acid catalysts, are important industrial processes in heterogeneous catalysis.[1–3] In the catalytic process, methanol is converted to a mixture of hydrocarbons (dimethyl ether, ethanol, methoxy and ethoxy groups *etc.*) on H-ZSM-5 zeolite. In most of the reaction mechanisms proposed for the MTG or MTO processes, surface methoxy group binding to the framework of the zeolite is believed to be the key intermediate that leads to the formation of the first carbon–carbon bond. Amongst the various surface analytic techniques, ^{13}C magic angle spinning (MAS) NMR is a particularly powerful tool for identifying the adsorbed species and intermediates, and eventually for illustrating the catalytic reaction mechanism.[1–3] In addition, the ^{13}C NMR chemical shift of the carbonyl carbon of adsorbed acetone is a particularly sensitive probe of the acid strength of various of solid acids (including zeolites)—considered to be closely associated to their catalytic activity.[4]

Generally, an unambiguous assignment of ^{13}C NMR chemical shifts in complex spectra is a non-trivial task. Quantum mechanics (QM) methods have proven to be useful in predicting the ^{1}H, ^{13}C and ^{15}N NMR chemical shifts of organic species, and thus would be of great help in the interpretation of experimental spectra.[5,6] However, the use of sophisticated QM methods to calculate the ^{13}C NMR chemical shifts of organic species adsorbed on zeolites is unfortunately either very expensive or sometimes even impossible because of the very large unit cell sizes of zeolites (typically containing hundreds of atoms). So far, little theoretical work has been reported that accurately reproduces the experimental ^{13}C NMR chemical shifts of organic species adsorbed on zeolites. Quantum mechanics/molecular mechanics (QM/MM) calculations were applied by Correa and Mota[7] to predict the ^{13}C NMR chemical shifts of alkoxide species adsorbed on HY and H-ZSM-5 zeolites. For the ethoxide species adsorbed on HY zeolite, a deviation of *ca.* 2 ppm from experimental measurement was achieved, whereas for the ethoxide species adsorbed on H-ZSM-5 zeolite, the deviation increased to as much as 10.3 ppm. In the latter case, the discrepancy for the ethoxide species was so large that its NMR chemical shift could not be distinguished from that of adsorbed ethanol.[7] Our previous study demonstrated that the combined ONIOM-GIAO method was an efficient one for calculating the NMR parameters for large systems, such as supramolecular assemblies of amino acids.[8]

In this communication, we present ONIOM-GIAO ^{13}C NMR chemical shift predictions for six adsorbed organic species, including acetone, methanol, ethanol and dimethyl ether (DME), adsorbed on the Brønsted acid site (denoted as HOZ). We also examine methyl and ethyl species adsorbed on the conjugated base site (denoted as OZ) of H-ZSM-5 zeolite.

The H-ZSM-5 zeolite was modelled by an $AlSi_{21}O_{63}H_{39}$ cluster model with hydrogen atoms saturating the extraneous bonds at the edge of the cluster and containing two 10-membered rings and one Brønsted acid site (Fig. 1). The structure parameters of H-ZSM-5 used in the calculations were extracted from the crystal structure data of the H-ZSM-5 zeolite.[9] In all ONIOM calculations, the active center ($O_3AlOHSiO_3$) and the adsorbed molecules were treated as the high-level layer, while the *rest* part of the model was

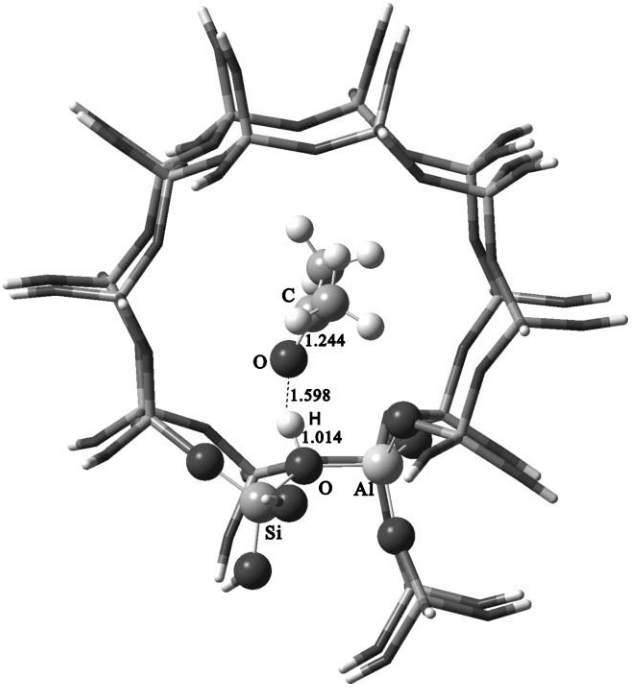

Fig. 1 The optimized geometry for acetone adsorbed on the Brønsted acid site (HOZ) of H-ZSM-5 zeolite. The high-level part is shown by a ball-and-stick representation and the low-level part by a tube model. Selected interatomic distances (Å) are also included.

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† Electronic Supplementary Information (ESI) available: Sample preparation and ^{13}C NMR spectrum of framework-bound ethoxy species on H-ZSM-5 zeolites. See http://www.rsc.org/suppdata/cc/b5/b501726b/
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treated as the low-level layer. For the geometry optimizations, the semi empirical AM1 method[10] was employed for the low-level treatment. The hybrid density functional B3LYP method[11] together with a standard DZVP2 basis set[12] were employed for the high-level treatment. To avoid losing the unique structure of zeolite H-ZSM-5, we performed partial optimization with the atoms of the high-level layer fully relaxed, and the *rest* atoms of the cluster model fixed at their crystallographic locations. The terminal O–H bonds were fixed at a length of 0.96 Å, oriented along the axis of the corresponding O–Si bond. The ^{13}C NMR chemical shifts were calculated using the ONIOM-GIAO (B3LYP/DZVP2: HF/6-31G) approach on the ONIOM (B3LYP/DZVP2: AM1) optimized structures. All calculations were performed using Gaussian03.[13]

The optimized geometry for acetone adsorbed on the Brønsted acid site of H-ZSM-5 zeolite is depicted in Fig. 1, while the optimized geometries (local views) of the other adsorbed species are shown in Fig. 2. It is noteworthy that the optimized geometries for the organic species predicted by our ONIOM (B3LYP/ DZVP2: AM1) calculations show some differences from those predicted by QM calculations using small cluster models. Taking the acetone–HOZ complex as an example (Fig. 1), our ONIOM optimization predicted a zeolite–OH bond length at the acidic site of 1.014 Å, a C=O bond length of 1.244 Å and an O–H distance of 1.598 Å between the carbonyl oxygen and the acidic proton. In contrast, the previous QM calculations using a smaller 8T cluster model predicted corresponding values of 1.043, 1.239 and 1.481 Å, respectively.[4] The discrepancy between the two predictions is obvious—with the maximum being ~0.1 Å. It is worth noting that the 8T cluster model is incapable of describing the long-range electrostatic interactions between the zeolite wall and the adsorbed species, whereas such interactions have been taken into account in our larger ONIOM model. Thus it can be expected that the ONIOM approach would provide a much better description of the complex geometries of organic species adsorbed on the zeolite.

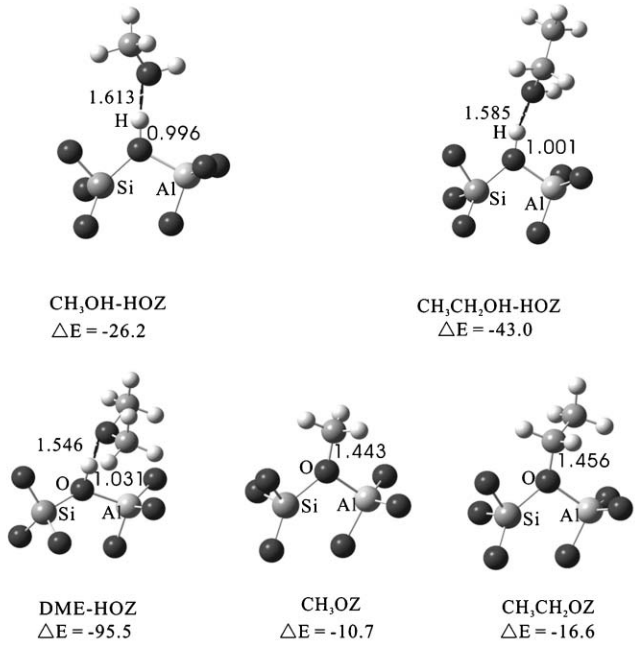

Fig. 2 Optimized geometries (local views) for various organic species adsorbed on H-ZSM-5 zeolite. Adsorption energies (ΔE/kJ mol^{-1}) predicted at the ONIOM(B3LYP/DZVP2:HF/6-31G) level are also given and selected interatomic distances (Å) included.

^{13}C NMR chemical shifts of the six organic species predicted at the ONIOM-GIAO(B3LYP/DZVP2:HF/6-31G) level are shown in Table 1. For comparison, available experimental data[1] as well as the theoretical values[4,7] for some of the adsorbed species previously predicted using much smaller cluster model are also listed in Table 1. It is clear that the ONIOM-GIAO calculations faithfully reproduce the experimental ^{13}C NMR chemical shift data for all the adsorbed organic molecules concerned, whereas the margins are substantial between the theoretical data, predicted using a small 2T cluster model, and the experimental data for the alkoxides adsorbed on H-ZSM-5 zeolite.[7] The differences between the results of our ONIOM-GIAO calculations and the experimental values range from 0–4.6 ppm for the six adsorbed species. However, the previous QM/MM method gave rise to differences of *ca.* 6 ppm and 10.3 ppm for the adsorbed methoxide and ethoxide, respectively.[7] As a result, it is difficult to discriminate between the ^{13}C NMR chemical shifts of methoxide (or ethoxide) species and those of the adsorbed methanol (or ethanol). It should be pointed out that the majority of the existing literature[1] reports an experimental ^{13}C NMR chemical shift of 56–59 ppm, rather than the 49.2 ppm, reported by Ivanova and Corma[2] and cited by Correa and Mota,[7] for the surface methoxide formed at the Brønsted acid site of H-ZSM-5 zeolite. The 49.2 ppm signal was usually assigned to strongly bonded methanol[1a] or methoxide formed on terminal SiOH[1a] or AlOH groups.[1g] Although a large 30T cluster model was employed by Correa and Mota in the geometry optimization, they used a small 2T cluster model for their chemical shift calculations.[7] Thus, the long-range electrostatic interaction might be included in the former case but ignored in the latter. In contrast, in our ONIOM-GIAO calculations, a 22T cluster model was employed for the ^{13}C NMR chemical shift predictions. It is noteworthy that the 2T cluster model prediction results were very close to experimental data for both the methoxide and ethoxide species adsorbed on HY zeolite.[7] One possible reason for this is that the channel diameter of HY zeolite (*ca.* 0.74 nm) is relatively large, and thus the long-range electrostatic interaction between the zeolite wall and the adsorbed species is not so pronounced as in H-ZSM-5 zeolite (having a channel diameter of *ca.* 0.53 nm).

Table 1 ONIOM-GIAO predicted and experimental ^{13}C NMR chemical shifts (ppm) of the organic species adsorbed on H-ZSM-5 zeolite

		Theoretical		
Species		This work	Previous	Experimental
CH$_3$OH–HOZ	C1	52.5		50.5–53[a]
CH$_3$CH$_2$OH–HOZ	C1	61.3		63[a]
	C2	19.1		17[a]
(CH$_3$)$_2$CO–HOZ	C2	223.9	238.4[b], 225.6[c]	223.7[a]
DME–HOZ	C1	60.3		59.5–62[a]
CH$_3$OZ	C1	56.7	50.3[d]	56–59[a]
CH$_3$CH$_2$OZ	C1	74.9	60.0[d]	70.3[e]
	C2	17.1	15.8[d]	17.1[e]

[a] Data extracted from ref. 1 [b] Predicted at the GIAO-RHF/QZP level (ref. 4). [c] Estimated by the GIAO MP2/QZP *vs.* RHF/QZP correlation (ref. 4). [d] Predicted by QM/MM method in ref. 7. [e] Our experimental data, see the Electronic Supplementary Information.

For the acetone–HOZ complex, our ONIOM-GIAO predicted ^{13}C NMR chemical shift is 223.9 ppm, very close to the experimental value (223.7 ppm),[4a] whereas the previous RHF calculations on a 8T model disagree by as much as 15 ppm.[4b] The MP2 method, which takes the electron correlation effects into account and accurately predicts NMR parameters, is very expensive and unfeasible for such a big system. Haw *et al.* had to estimate the MP2 ^{13}C NMR chemical shift of acetone adsorbed on H-ZSM-5 zeolite based on the RHF prediction by using a linear correlation $\delta_{\mathrm{MP2}} = 1.12\delta_{\mathrm{RHF}} - 42.1$, giving a prediction that disagreed by nearly 2 ppm.[4b]

It is notable that the predicted ^{13}C NMR chemical shifts of methanol and ethanol adsorbed on the Brønsted acid sites by hydrogen bonding interactions are quite similar to their liquid-state values.[14] In contrast, for the methoxy and ethoxy surface species, *i.e.*, CH_3OZ and CH_3CH_2OZ, their predicted ^{13}C NMR chemical shifts are *ca.* 10 ppm larger than their liquid-state values. The formation of these surface species, upon dehydration of their corresponding adsorbed species CH_3OH–HOZ and CH_3CH_2OH–HOZ, are thermodynamically favorable with predicted exothermicities of ~13 kcal mol^{-1}.

In summary, we have employed a large cluster model in combination with the ONIOM-GIAO method to predict the ^{13}C NMR chemical shifts for six surface organic species adsorbed on H-ZSM-5 zeolite. Our ONIOM-GIAO calculations successfully reproduced the experimental data, demonstrating that an approach involving the suitable inclusion of long-range electrostatic interactions in the cluster is indispensable to ensuring not only better descriptions of geometries, but also accurate predictions of the ^{13}C NMR chemical shifts of organic species adsorbed on the zeolite. The results we have reported will be helpful in the identification of the catalytic processes involved in more complicated chemical systems of industrial importance.

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